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ON THERMO-ELECTRIC HETEROGENEITY IN CERTAIN ALLOYS, ESPECIALLY GERMAN-SILVER.

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Purpose and General Plan of the Investigation.

In a paper on "Thermal and Electrical Effects in Soft Iron," published in these Proceedings for May, 1905, by the authors of the present paper, together with Mr. E. P. Churchill, brief account was given, at pages 42–45 and 54, of the construction and calibration of two sets of copper and german-silver thermo-electric couples, which will hereafter be referred to as A, B, C, D and A_1, B_1, C_1, D_1, respectively. The study of these couples, all of which were made from one original piece of copper and one original piece of german-silver, was confined to the temperature range 0° C. to 100° C., as the experiments on soft iron, to which experiments the thermo-electric couples were contributory, lay within this range.

It was intimated, however, in the paper already mentioned, that similar experiments on iron through the interval from 100° C. to 200° C. would presently be undertaken, and with a view to this work a study of copper and german-silver thermo-electric couples through this higher range became necessary. It was hoped, too, that these proposed calibration tests could be carried out with such accuracy and thoroughness as to add something valuable to our knowledge of the general behavior of such thermo-electric couples, the permanence or variability of quality in any particular couple, for example, or the causes and magnitude of the differences between couples made, as nearly as may be, of the same materials and in the same way. These secondary purposes of the investigation have been in some measure fulfilled, through variations of experimental conditions which were not at first planned and which seem to us worthy of being described with some detail.

More strictly, the higher limit of temperature now proposed was the boiling point of naphthalin under atmospheric pressure, about 218° C.

Furthermore, following the advice of Professor J. M. Crafts, who gave us every facility to copy the apparatus which he has used in his comparative study of the behavior of boiling water and boiling naphthalin under various pressures, we determined to employ for calibration purposes all the way from 100° C. to 218° C. the saturated vapors of water and naphthalin, respectively, using the water at high pressure and the naphthalin at low pressure for the temperatures intermediate between the limits.

General Summary.

1. All of the german-silver wires used in the experiments of this paper, with the exception of those taken for a certain experiment to be described below, were cut from one continuous strand described by the dealer from whom it was procured as containing 18 per cent of nickel. Special chemical analysis of a specimen of this wire, taken unannealed, gave as the composition:

Copper,	58.76 per cent.
Zinc,	22.54 " "
Nickel,	17.44 " "
Iron,	1.29 " "

Analysis of the annealed wire resulted as follows:

Copper,	63.19 per cent.
Zinc,	18.48 " "
Nickel,	17.59 " "
Iron,	0.71 " "

The diameter of this wire was about 0.02 cm.

2. Pieces of this wire were annealed by heating to incandescence by an electric current and keeping them in this state for some seconds in free air, the ends of each piece during the annealing being kept at the same level, so that the heated wire had approximately a catenary shape. After cooling, the wires were found to have suffered very little, if any, permanent extension. The strength of current used was usually about 3.5 amperes, but it was not very carefully measured. The state of incandescence probably lasted two or three times as long in some cases as in others.

3. Couples made from copper, also 0.02 cm. in diameter, and pieces of german-silver annealed as in (2), appeared to differ from each other in sensitiveness, when new, rather less than 0.5 per cent; but after

four such couples had been used for some time, with repeated heatings of the junctions to a temperature of 218° in air (sometimes contaminated by vapors of various kinds) the difference appeared to be greater, amounting in one case to slightly more than 2 per cent. These couples had been subject to many vicissitudes of handling; but no satisfactory explanation of the increase in their range of sensibility can at present be given; it is possible that the first estimate of this range was too small and the last too large.

4. The german-silver wires used in these couples were about 1.5 m. long. When one junction of such a couple was immersed to a depth of 50 cm. in air heated to the neighborhood of 180° C. and the other to a like depth in air at a temperature near 140° C., the intermediate part of the german-silver wire being exposed to the air of the room with no other shield than the wall of a glass tube within which it was enclosed, the mean electromotive force per degree of the couple sometimes changed as much as 5 per cent when the temperature interval was reversed, the junction which had been in the 180° place being put into the 140° place and *vice versa*. All attempts to explain such discrepancies as due to local electromotive forces in parts lying outside the german-silver failed. Attempts to account for them by means of local peculiarities in the german-silver wire led to the experiments described in the next three sections of this summary.

5. Four couples, each made from a single piece of annealed german-silver by leaving one part of it straight while the other part was formed into an elongated spiral wound on a cylinder about 1 cm. in diameter, were tested. The mean electromotive force of the four appeared to be about 0.07 per cent of the electromotive force of a couple made of german silver and copper, the spiral wire being thermo-electrically a little farther away from copper than the straight wire is. No great confidence should be placed in the numerical accuracy of this result.

6. Four couples, each made from a single piece[1] of annealed german-silver by leaving one part of it unchanged while the other part was stretched permanently 10 per cent, were tested. As a mean result it was found that such couples have an electromotive force about 0.6 per cent as great as that of a copper and german-silver couple, the stretched german-silver being thermo-electrically farther removed from copper than the unstretched wire is.

[1] These four pieces were from the same spool of wire (all called 18 per cent nickel) as the others, but not from the same strand.

If in the testing of the (copper)-(german-silver) couples a part of the german-silver wire lying in the place of steepest temperature gradient, just outside the entrance to one of the heating vessels, happens to have been severely stretched, it may give rise to such a discrepancy of behavior as that noted in (3) above. But, as such discrepancy was found in couples the german-silver of which had been carefully guarded from any serious stretching, it seemed necessary to look further for a satisfactory explanation.

7. The application of the sharp edge of a lump of ice to a straight piece of german-silver wire exposed to the air of the room, this application being many centimeters distant from either end of the wire, developed a perceptible local electromotive force, which frequently changed its sign as the point of contact was moved, 1 cm. at a time, along the wire. The cooling produced by the ice was plainly perceptible at a distance of 1.5 cm. along the wire from the point of contact, though the cooling at 1 cm. from the contact point is perhaps not more than one third as great as at this point. We may regard the ice test as showing that the mean thermo-electric quality of the wire for a distance of perhaps 1 cm. in one direction from the point of contact is perceptibly different from that of the corresponding piece lying on the opposite side of the point of contact.

Annealing was found to increase the range of thermo-electric heterogeneity of the wire and to change the local distribution of this heterogeneity.

Stretching annealed wire to a permanent extension of 10 per cent made very little change in the range or distribution of the thermo-electric heterogeneity. Reannealing a wire which had been thus stretched changed again the distribution of its peculiarities and increased still further the range of these peculiarities. In a wire so treated, contact at one point with an edge of ice developed an electromotive force about 0.2 per cent as great as that which would have been developed by touching the ice to a junction of copper with german-silver.

These tests show that there may be in straight, recently annealed german-silver wire local differences of thermo-electric quality which may cause serious error if a copper and german-silver couple is used to measure a small difference between two high temperatures, the intermediate part of the german-silver wire being exposed to air at the ordinary temperature of a room. To avoid error from this source the practice of reversing the temperature interval of the junctions should be followed whenever this is practicable.

8. By keeping the intermediate parts of the german-silver wires not far below the temperature of the cooler junction in the calibration tests, the change of sensitiveness observed on reversing the temperature interval of the junctions, about 40°, was reduced from an average of about 3 per cent to an average of about 0.8 per cent.

9. As a result of all the calibration work done on thermo-electric couples of the kind described above it appears that, if we take 2100×10^{-8} volt as the mean "thermo-electric height," electromotive force with 1° difference of temperature of junctions, at 100° C., and if we take 4.8×10^{-8} as the rate of increase per degree rise of temperature, we shall get values which will not at any point between 0° and 218° differ as much as 1 per cent from the most probable value which we have for that point.

10. A piece of manganin wire subjected to the ice test described in (7) behaved very much as the german-silver wire did, in magnitude of local electromotive forces developed, in effect of annealing, and in non-effect of stretching.

11. A piece of constantin wire subjected to the ice test showed much smaller local electromotive forces than did german-silver and manganin, perhaps one fifth as great, and annealing, although it affected the distribution of the local peculiarities, did not sensibly increase their magnitude.

Annealing this constantin wire, which had been hardened by drawing down from 0.051 cm. to 0.036 cm. diameter, changed its "thermo-electric height" with respect to copper about 1.5 per cent, the annealed wire being nearer to copper thermo-electrically than the hard-drawn wire.

12. As the thermo-electric height of manganin with respect to copper is two or three times as great as that of german-silver with respect to copper, at ordinary temperatures, as, further, annealing seems to make less proportional difference in constantin than in copper, and as, finally, the thermo-electric heterogeneity of constantin appears to be relatively less than that of german-silver, it would seem that couples of constantin with copper are to be preferred to couples of german-silver with copper for ordinary use.

It must be remembered, however, that the experiments here described relate to one kind only of german-silver and to one specimen only of constantin.

Detailed Account of the Work.

Couples A_2, B_2, C_2, and D_2.

Four new copper and german-silver couples, which will be called A_2, B_2, C_2, and D_2, were made July 5, 1905, from the same pieces of copper and german-silver which had furnished the materials for the couples previously mentioned. Each wire was about 0.02 cm. in diameter. Each german-silver wire, about 160 cm. long, was annealed as the wires for previous couples had been, by carrying for a few seconds a current of about 3.5 amperes, which heated it to incandescence except at the ends, which were afterward cut off, leaving the wire about 150 cm. long. Each annealed wire was made to extend through two glass tubes, each about 50 cm. long and 0.3 cm. in diameter of bore, and each end of the wire, after being cleaned with emery paper, was then tightly twisted with a copper wire for a distance of about 0.5 cm. The junctions thus made were heated in an alcohol flame and flowed with a silver solder, the borax used in this operation being afterward removed, so far as was practicable, from the wires.

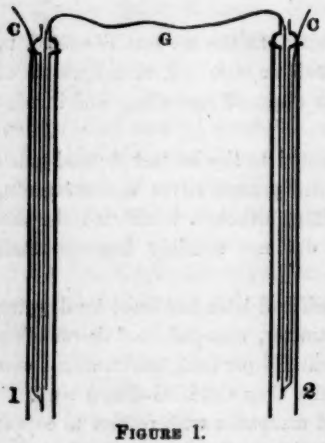

Figure 1.

The small glass tubes were next placed in glass tubes about 54 cm. long and 1 cm. in diameter, as in Figure 1, where C and C represent the copper wires and G represents the german-silver wire. One of these larger glass tubes, with its contents, was now placed in a vessel of peculiar construction, due to Professor Crafts, where it could be raised to the temperature of the vapor given off from distilled water boiling at any required pressure, but without coming into direct contact with this vapor. The other large glass tube, with its contents, was similarly placed in a similar vessel containing the saturated vapor of naphthalin, the purest that Eimer and Amend could furnish, at any required temperature. The steam temperatures were found from the steam pressures, measured by a mercury gauge, by means of Peabody's Tables, which are based, of course, on Regnault's observations. The naphthalin temperatures were calculated from the naphthalin vapor pressures by

means of a formula furnished us by Professor Crafts, which formula has not yet been published.

Observations.

Observations were sometimes made with junctions 1 (see Figure 1) in the naphthalin pot and junction 2 in the steam pot, and sometimes with the opposite arrangement. The first was called "the parallel" arrangement; the second, the "crossed" arrangement. A complete run for any one day included a set of observations made on each couple, with the parallel arrangement, and another similar set made with the crossed arrangement, the temperatures being kept, as nearly as might be, constant during the whole run.

If on one day the observations were taken first with the "parallel" arrangement and then with the "crossed" arrangement, on the next day of work, as a rule, the observations were taken first with the "crossed" arrangement and then with the "parallel" arrangement.

The thermo-electric current from each of the four couples was observed by means of an armored Siemens-Halske galvanometer, the sensitiveness of which was at first taken before beginning the observations with the four couples, between the two sets of observations, and after the second set. This sensitiveness was found to vary but little from hour to hour, or even from day to day; and after a time the between-sets test was often omitted. All the resistance coils used during this work were carefully compared with international-standard-ohm coils, and were found correct to within one tenth of one per cent.

The usual order of observations was as follows, (3–2), for example, meaning three galvanometer deflections in one direction and two in the other direction: A (3–2), B (3–2), C (3–2), D (5–4), C (3–2), B (3–2), A (3–2), a reversal of the couples from "parallel" to "crossed" or *vice versa*, then a wait of one hour for equilibrium of temperature to re-establish itself, then, as before, A (3–2), B (3–2), C (3–2), D (5–4), C (3–2), B (3–2), A (3–2).

Observations of the pressure gauges, when artificial pressure conditions were used, and of the barometer, accompanied these galvanometer observations and gave data for calculating the temperatures of the junctions.

The following summary of the results of the observations made July 21, 1905, is a fair sample of the summaries usually obtained. The numbers given under "Sensitiveness" are galvanometer deflections observed on reversal of a current of known constant strength used in getting

the sensitiveness of the galvanometer. The numbers given under A_2 or B_2, etc., are the galvanometer deflections observed on reversal of a commutator in the thermo-electric circuit containing the couple referred to:

Time.		Sensitiveness.
1:15	P. M.	21.20
3:05	"	21.20
5:25	"	21.19
	Mean	21.20

			A_2	B_2	C_2	D_2	Temperatures.	
1:40	P. M.		19.84	19.66	20.03			
		"Parallel"				19.80		
2:55	"		19.86	19.67	20.04		180°.36	140°.12
			19.85	19.67	20.04	19.80		
4:05	"		19.68	19.85	19.36			
		"Crossed"				19.74		
5:20	"		19.71	19.85	19.38		180°.36	140°.07
			19.70	19.85	19.37	19.74		
		Means . .	19.77	19.76	19.71	19.77	180°.36	140°.10

Mean of all = 19.75 Diff. = 40°.26

These data yield the following values:
Mean total e. m. f. = 958×10^{-6} volt,
" e. m. f. per degree, between 140°.10 and 180°.36 = 2378×10^{-8} volt.

Putting aside, for the present, consideration of the absolute values here indicated, we may observe a number of comparative features which are of interest:

First, that the smallness of the difference between the earlier and the later deflections obtained with the same couple in each of the two groups "parallel" and "crossed" is good evidence that practical thermal equilibrium was attained before the beginning of each of these two groups of observations. Even the slight tendency here observed toward increase of the deflections with progress of time is greater than was usually evident.

Second, that in each of the two groups, "parallel" and "crossed," considerable differences between the deflections yielded by different

couples are to be seen, the extreme difference, in the "crossed" group, being more than 2 per cent of the mean deflection. These differences are not to be accounted for by differences of resistance of the different couples, for each had a resistance very near 16 ohms, while the resistance of the rest of the circuit, into which each couple was introduced in turn, was more than 1000 ohms. Nor are the differences in question to be regarded as purely accidental, in the sense of having no tendency to recurrence. Taking the observations of the five days on which the four couples here considered were tested with temperatures near 140° and 180° we get, as means:

	A_2		B_2		C_2		D_2
"Parallel"	19.82		19.64		19.93		19.78
		>0.03		>0.30		>0.36		>0.05
"Crossed"	19.79		19.94		19.57		19.83
	19.81		19.79		19.75		19.81

Here we have as the order according to magnitude of deflections: "parallel," C > A > D > B, "crossed," B > D > A > C, just as on July 21, the case cited in detail above. The mean range of variation through the five days now considered was about 1.6 per cent for the "parallel" and about 2 per cent for the "crossed" arrangement.

Third, that a couple which gives a deflection larger than the mean with the "parallel" arrangement is likely to give a deflection smaller than the mean with the "crossed" arrangement, and *vice versa*, so that differences of the kind mentioned in the preceding paragraph are very small among the individual means, of "parallel" and "crossed" taken together, yielded by the various couples. The greatest difference on July 21 was less than $\frac{1}{3}$ per cent of the mean deflection, and the greatest difference in the five-day means given above is the same, 6 parts in nearly 2000.

Fourth, that the mean "parallel" deflection for July 21, which is 19.84, exceeds the mean "crossed" deflection for the same day by nearly 1 per cent of the mean deflection. It is to be observed, however, that the mean "parallel" deflection and the mean "crossed" deflection of the five-day summary are almost exactly equal, being respectively 19.79 and 19.78.

As an example of the daily summaries obtained when the junction temperatures were 100° and 218,° approximately, the following, for July 25, will serve:

Time.			Sensitiveness.
11:45	A. M.	. . . . .	21.20
2:30	P. M.	. . . . .	21.21
5:05	"	. . . . .	21.18
		Mean	21.20

			A_2	B_2	C_2	D_2	Temperatures.
12:35	"	"Crossed"	19.63	19.69	19.52		
						19.71	
1:24	"		19.60	19.71	19.53		217°.9 99°.9
			19.62	19.70	19.53	19.71	
4:15	"	"Parallel"	19.69	19.64	19.71		
						19.70	
4:57	"		19.68	19.62	19.72		217°.9 99°.9
			19.69	19.63	19.72	19.70	
		Means . .	19.65	19.67	19.62	19.71	217°.9 99°.9

Mean of all = 19.66 Diff. = 118°.0

These data yielded the following values:

Mean total e. m. f. = 2807×10^{-6} volt.

" e. m. f. per degree, between 99°.9 and 217°.9 = 2379×10^{-8} volt.

Examining this summary as we have examined that of July 21, we find:

First, that, as before, practical equilibrium of temperature was maintained throughout the course of observations.

Second, that in each of the two groups, "parallel" and "crossed," the differences between the deflections yielded by different couples are considerably less than were the corresponding differences on July 21, the greatest difference now found being rather less than 1 per cent of the mean deflection. This greater uniformity is probably due to the greater interval of temperature used on July 25, 118° instead of the 40.3° of July 21. Taking a summary of the deflections yielded by the four couples on the four days when they were tested with temperatures near 100° and 218° we get:

	A_2		B_2		C_2		D_2		Mean.	
"Parallel"	19.60		19.56		19.63		19.62		19.60	
		>0.02		>0.13		>0.13		>0.03		>0.02
"Crossed"	19.62		19.69		19.50		19.65		19.62	
	19.61		19.63		19.57		19.64		19.61	

Here, too, the greatest difference observed in either of the two groups, "parallel," and "crossed," is a very little less than 1 per cent of the mean, 19 parts in nearly 2000.

Third, that, as before, a couple which gives a deflection larger than the mean with the "parallel" arrangement, is likely to give a deflection smaller than the mean with the "crossed" arrangement, and *vice versa*, so that differences between the individual means of "parallel" and "crossed" taken together, yielded by the various couples, are small, the greatest being 9 parts in nearly 2000 for July 25 and 7 parts in nearly 2000 for the four-day summary.

Fourth, that the mean "parallel" deflection for July 25, 19.68 +, is a little greater than the mean "crossed" deflection, 19.64, for the same day. In the four-day summary, however, we find the mean "parallel" deflection to be 19.60, while the mean "crossed" deflection is a very little greater, 19.62.

On one day, July 5, and on that day only, observations were made with the interval of temperature from 100° to 136°, approximately. The summary for the individual couples with this interval for this one day is as follows:

	A_2	B_2	C_2	D_2	Mean.
"Parallel"	15.21	15.19	15.34	15.27	15.25
	>0.09	>0.16	>0.07	>0.02	>0.04
"Crossed"	15.30	15.35	15.27	15.25	15.29
	15.26	15.27	15.31	15.26	15.27

It seems hardly worth while to discuss this summary in detail at present, though it will be referred to later.

Taking the five-day summary for the interval 140° to 180° with the four-day summary for the interval 100° to 218°, and still postponing discussion of the absolute values of electromotive force found with these intervals, we reach the following conclusions from the data and the discussion already given:

1. That with the four couples A_2, B_2, C_2, D_2, made in the same way from the same materials, a maximum range of electromotive force amounting to about $\frac{1}{2}$ per cent of the mean electromotive may be expected in a thorough test with any interval of temperature between 100° and 218°. The one day's work with the interval 100° to 136° is in complete accord with this conclusion.

2. That the couple C_2 is sufficiently exceptional in its behavior to demand especial attention. This couple gave the lowest mean deflection for the 100°–218° interval and also for the 140°–180° interval; for the 100°–136° interval it was still exceptional, but it gave here the largest mean deflection. On the whole, too, the difference between "parallel" and "crossed" was larger with this couple than with any other.

All attempts to account for such variations and peculiarities by causes lying outside the german-silver wire were unsuccessful. Looking for possible causes of difference in the german-silver wires we naturally gave much thought to the rather sharp bends which, with the arrangement shown in Figure 1, inevitably occurred just above the tops of the glass tubes through which these wires ran. It was thought that these bends, by introducing some change of quality in the wires at a place where the gradient of temperature is large, might account for the differences noted. Tests made by heating or cooling the various wires at or near the bends in question did not, it is true, fully justify this theory; but in order to give it a fuller trial it was determined to make a new set of four couples and to support the german-silver wire of each couple in such a way that it would be subject to no violent or greatly variable bends in its course from one heating pot to the other.

Couples A_3, B_3, C_3, and D_3.

The four new couples, made from the same materials as the others and in substantially the same way, will be called A_3, B_3, C_3, and D_3, respectively. The new method of mounting is indicated by Figure 2, in which S is a wooden splint to which are lashed the horizontal ends of the small glass tubes containing the german-silver wire, these ends being connected by a short rubber tube. Corks fitting snugly on the outer glass tubes were lashed to the upper parts of the smaller tubes, so that when the splint S was raised the whole system of protecting tubes was raised with it. The greater part of each small tube above the larger glass tubes was exposed freely to the air of the room. The upper part of the larger tubes was surrounded by loose asbestos, which, as before, lay on the covers of the pots to a depth of about 3 cm.

The result of this attempt to improve the conditions of experiment was disappointing. With the new arrangement and the new set of couples the differences between the behavior of different couples and the differences between "parallel" and "crossed" with the same couple were greater in general than we had found with the old set of couples, A_2,

B_2, etc. Going into details, and looking all the time for the causes of descrepancies, we found that couple C_3, like couple C_2 in the quartet of couples previously studied, was the worst of its set, giving the lowest electromotive force and showing the greatest difference between the "parallel" and the "crossed" condition.

As C_3 occupied in the pots the same place which C_2 had before occupied, we naturally suspected that there might be something peculiar in the C part of one or the other of the pots. Moreover, moisture was sometimes seen in the upper part of the glass tube containing the german-silver of C_3, which suggested that there might be a small leak of steam into the tube containing one junction of this couple. Accordingly, on September 25 we changed all the couples about, putting A_3 where D_3 had been, and *vice versa*, and B_3 where C_3 had been, and *vice versa*. The effects, such as they were, of this change may be inferred from the following comparative set of numbers, those for September 23 being obtained before, and those for September 25 after, the transposition just described:

	A_3	(P − C)	B_3	(P − C)	C_3	(P − C)	D_3	(P − C)
Sept. 23	20.30	(+0.27)	20.17	(+0.16)	20.02	(−0.19)	20.23	(−0.04)
" 25	20.30	(+0.36)	20.14	(+0.36)	20.08	(+0.52)	20.14	(−0.25)

The deflections here given for the two days are reduced to like conditions of galvanometer sensitiveness and temperature interval, so that they are strictly comparable. Under (P − C) is given the "parallel" deflection *minus* the "crossed" deflection. The mean deflection is 20.180 for September 23 and 20.165 for September 25, an insignificant difference. Couple C_3 gives the smallest deflection on each day; its (P − C) was larger on the second day than on the first, and of the opposite sign, but its (P − C) for September 23 was exceptionally small and unusual in sign. Couple B_3, which had been put into the place of C_3, showed no change that appeared very significant.

On September 26, also, the couples were used in their interchanged positions, but with an interval of temperature different from that used September 23 and 25, and on this day also C_3 gave as usual a deflection about $\frac{1}{4}$ per cent below the mean given by the four couples, while B_3 gave, as usual, a deflection very near this mean.

On the whole, then, it seems probable that the low electromotive force of the two C couples was an accidental coincidence, not due in any discoverable measure to their position in the apparatus. Never-

theless, to avoid possible trouble from a possible minute leakage of steam, it was determined to seal at the bottom the large glass tubes which served as a shield for the junctions.

At the same time a change was made in the manner of connecting the small glass tubes at their tops. The couples were removed temporarily from these tubes; the splints and rubber tube connectors shown in Figure 2 were abolished; and the two small glass tubes for each couple were now joined directly to each other in one piece, as in Figure 3. Then the couples were replaced in the tubes. In this change little or no care was taken to distinguish between the two ends of each couple, and it appears that D_3 was turned about in its replacement, so that for this couple "parallel" afterward corresponded to the same orientation of the couple to which "crossed" had previously corresponded; for the (P — C) of this couple was consistently + after the change, whereas it had usually been — before. This change was made between the observations of September 27 and those of September 28. A comparative summary for September 26 and September 28 is here given, the interval of temperature on both days being approximately 140°–180°.

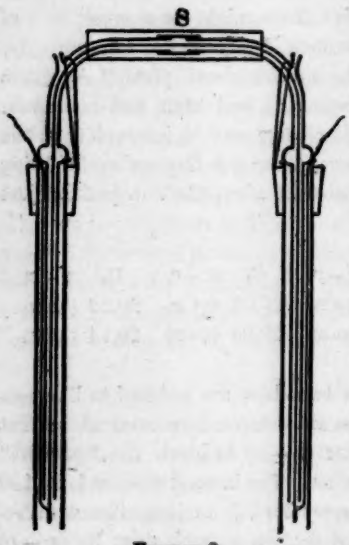

FIGURE 2.

	A_3	(P — C)	B_3	(P — C)	C_3	(P — C)	D_3	(P — C)
Sept. 26	19.88	(+0.74)	19.66	(+0.71)	19.61	(+1.08)	19.65	(−0.34)
" 28	20.00	(+0.62)	19.83	(+0.08)	19.74	(+0.61)	19.84	(+0.69)

On the whole, the results of the overhauling given to the apparatus in the change from the arrangement of Figure 2 to that of Figure 3 were unimportant so far as harmony of performance is concerned.

On September 27, still under the impression that the differences of behavior of the different couples and the (P — C) values of the individual couples might be accounted for by the gradients of temperature in the bent parts of the german-silver wire above the pots, we tried

the experiment of raising all of the couples about 20 cm. higher than usual, with the object of getting the bent part of the german-silver wires far enough away from the top of the pots to have them in a region of nearly uniform temperature. With the same object in view we placed shields of asbestos to protect these parts of the wire from the heat given off by the pots and the tubes above them. All this was done in the hope of more uniform performance by the different couples. How little ground there was for this hope may be seen from the following summary of the series of observations made with this arrangement, although the observations at the last went so badly that the series was not completed in the usual way:

	A_3 (P − C)		B_3 (P − C)		C_3 (P − C)		D_3 (P − C)		Mean (P − C)	
P	20.61	+ 1.84	20.21	+ 2.01	19.90	+ 1.57	19.63	+ 0.87	20.09	+ 0.157
C	18.77		18.20		18.33		18.76		18.52	
	19.69		19.21		19.12		19.20		19.31	

These observations of September 27, taken in connection with what had gone before, told strongly against the theory which attached great importance to the bent parts of the german-silver as a source of variation and irregularity, and after the experiments of September 28 and 29 had shown that moisture had probably exerted no appreciable influence on the performance of the couples, it seemed probable that the cause of the irregularities noted must be looked for in differences of condition in the straight parts of the german-silver wires. Accordingly we decided to look for such differences by direct experiment; but we thought it best to make, before this study was undertaken, a direct experiment on the change which moderately sharp bending makes in the thermo-electric condition of german-silver wire.

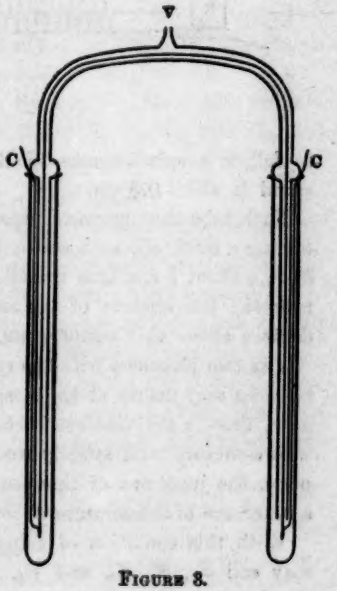

FIGURE 3.

On the Effect of bending German-Silver Wire.

As we had used, in the research on the Thomson effect in iron, spirals of german-silver wire wound on a cylinder 1 cm. in diameter, assuming that the bending produced no important change in the thermo-electric performance of the wire, investigation of the effect of this particular curvature seemed now especially appropriate, even if somewhat belated.

Four pieces, each 150 cm. long, of just such annealed german-silver wire as had been used in making our thermo-electric couples, were taken, and each was mounted on a glass tube about 1 cm. in diameter and 16 cm. long in the manner indicated by Figure 4. C and C are copper wires lashed to the cork K_1 and soldered to the german-silver wire, which, beginning at A, enters the tube through a hole in the side and runs straight to the farther end, where it emerges under the cork K_2

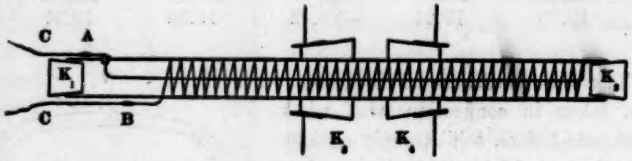

FIGURE 4.

to follow a spiral course to B. The distance between turns of the spiral is about 0.3 cm.

Each tube thus prepared was made to connect two metal vessels containing a thick oil, each end extending through a tight-fitting cork, K_3 or K_4, about 5 cm. into the oil. One body of oil was kept at or very near the temperature of the room; the other was heated to 15 or 20 degrees above this temperature.

The two junctions with the copper being near together in one body of oil were very nearly at the same temperature. The arrangement really gave, then, a thermo-electric couple consisting of straight german-silver wire combined with spirally wound german-silver wire in one continuous piece, the junctions of this couple being in the two vessels of oil with a difference of temperature of some 15 or 20 degrees.

With this condition of things, tests of the four couples, which we may call S_1, S_2, S_3, and S_4, respectively, were made on two days, October 6 and 7. On each day S_1 and S_2 gave deflections in one direction and S_3 and S_4 gave deflections in the opposite direction. Dividing

by 4 the algebraic sum of these deflections and comparing them with the effect obtained with a german-silver and copper couple having a like interval of temperature, we found that, on the average, the spiral-straight german-silver couples had a thermo-electric force about $\frac{1}{300}$ as great[2] as that of the german-silver and copper couple, the spiral wire being, apparently, a little farther removed, in thermo-electric quality, from copper than the straight german-silver is.

This seems to show that moderately sharp bending (with a radius of 0.5 cm.) is not very injurious in the ordinary thermo-electric use of german-silver wire. It is to be noted, however, that, if a german-silver and copper couple is used to measure some very small interval of temperature, 0°.1, for example, and if in some bent part of the german silver there is a very much greater interval of temperature, 15°, let us say, such a difference of quality in this bent part as we have inferred from our experiments on the spirals would make an error of 10 per cent in the estimation of the 0°.1 interval. But if in such a case it is practicable so to vary the conditions of the experiment as to reverse the small temperature-interval to be measured, without at the same time changing materially the gradient of temperature in the german-silver wire, error caused by the non-homogeneity of this wire will be practically eliminated from the result of the combined observations.

It seems unlikely that the bends in the upper parts of the german-silver wires of the couples A_2, B_2, C_2, D_2, or A_3, B_3, C_3, and D_3, had any important effect in the performance of these couples.

Thermo-electric Heterogeneity in Straight German-Silver Wire.

We now return to the question whether in a straight piece of german-silver wire there is any discoverable thermo-electric heterogeneity.

After some tentative experimenting the arrangement indicated, as seen from above, by Figure 5 was adopted: G G is the german-silver wire, held nearly straight but with no great tension by the screw-heads S and S ; C and C are copper wires soldered to the german-silver, the junctions being immersed in glass vessels containing oil at the temperature of the room; M M is a meter-rod.

The copper wires being connected with the terminals of a galvanometer, the sharp edge of a piece of ice was placed in contact with the under side of the german-silver wire, as in Figure 6, opposite the 25 cm.

[2] This electromotive force is too small to be with certainty attributed to the bending.

mark of the meter-rod. The result was usually a small deflection of the galvanometer needle, which deflection remained fairly constant until the ice was withdrawn, when it soon disappeared. The ice was then placed opposite the 26 cm. mark and the deflection was noted. In this way progress was made, by 1 cm. stages, until the 75 cm. mark was reached. Then a return set of observations was made, beginning at the 75 cm. mark and ending at the 25 cm. mark, with 1 cm. stages.

For any one point the return observation usually showed a deflection of the same sign and the same order of magnitude as the deflection shown by the forward observation. The mean of the two deflections was taken for each point examined, and the mean deflections, or quantities proportional to them, were plotted on co-ordinate paper, distances along the wire being measured on a horizontal line and the deflections being represented by vertical distances above or below this horizontal line.

FIGURE 5.

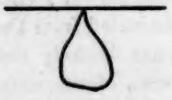

FIGURE 6.

Through the points thus placed a curve was drawn free hand, which indicates roughly the variations of thermo-electric condition revealed by progressive observations along the wire. C_1 in Figure 7 is the figure thus obtained with an unannealed specimen, which we will call No. 1, of wire from the same piece which has furnished the german-silver of our couples. The maximum height of this curve, which occurs over the 12 cm. point, corresponding to the 37 cm. point of the wire as shown in Figure 5, indicates an electromotive force of 16×10^{-6} volt, approximately, as a result of touching the wire with ice, when the room temperature was about 18° C.

The curve in question crosses the median line, of no electromotive force, 22 times in the 50 cm. of wire investigated. There was no obvious reason for these alternations of thermo-electric effect, or indeed for any thermo-electric effect. The wire, in the part tested, was free from any serious looking kinks or other imperfections.

After the data for curve C_1 had been obtained the wire was annealed in the usual way, without being released from the screws S and S, Figure 5, which held it upon the experimental rack. As the annealing

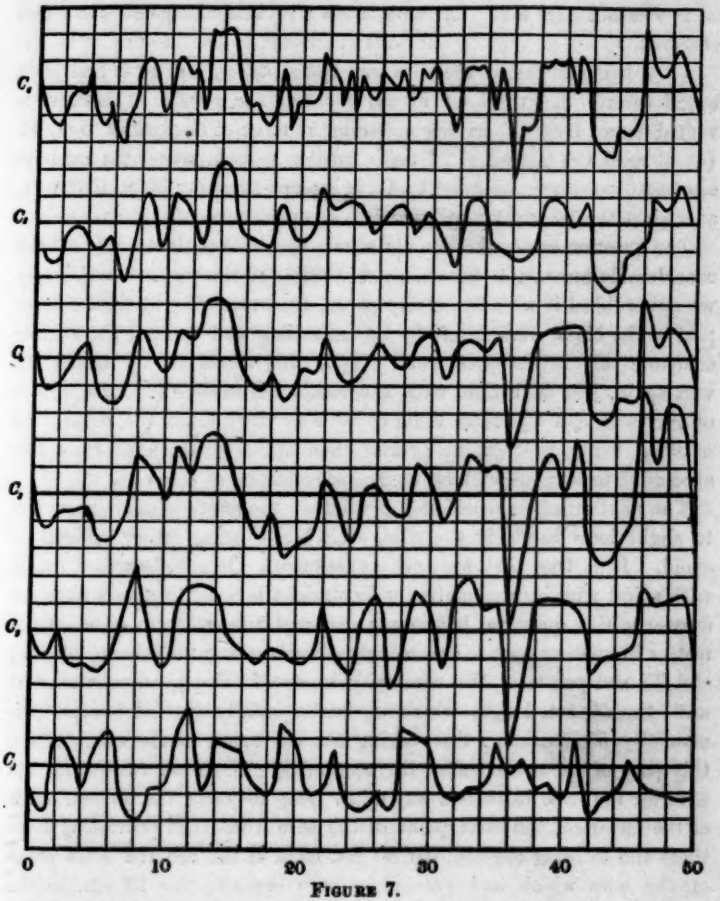

FIGURE 7.

appeared to leave the wire a little slack after cooling, the left-hand S was loosened and the wire was drawn a trifle till it became moderately taut once more; but later, and before any more observations were made on it, the left-hand S being loosened again, the wire was slackened to

the same state, as nearly as we could tell, in which the annealing had left it. These details are mentioned for the reason that it was important to test after the annealing the same points, as nearly as might be, which had been tested before the annealing; for sometimes a movement of one or two millimeters along the wire made a serious change in the effect observed.

After being annealed the wire was tested again, just as it had been tested before. Curve C_2 of Figure 7 shows the result. This curve is very different from C_1, having a smaller number of changes of sign, 17 (or at most 19) instead of 22, and a greater vertical range, the greatest electromotive force indicated by C_2 being aproximately 30×10^{-8} volt, as against the 16×10^{-8} volt which is the maximum of C_1.

The question arose whether the effects observed could be due in any considerable measure to the surface condition of the wire. Accordingly we now rubbed it with fine emery paper, thus removing at least a large part of the black coating left by the annealing and making the surface comparatively bright once more. After this treatment we tested the wire again, just as before, with the result shown by C_3. Comparison of curves C_2 and C_3 shows them to be very much alike, the differences of detail being, perhaps, no greater than might be expected from two successive tests made without change of condition of the wire.

The next question considered is whether the effects observed are due to slight local bends in the wire, such bends being rather difficult to avoid. It is true that previous experiments, already described, made with spiral wire in combination with straight seemed to give a negative answer to this question, but it was easy and interesting to come at the matter in another way. Accordingly, after marking the 25 cm., 50 cm., and 75 cm. points of the wire with knots of thread, we stretched it until the 50 cm. length which we had especially studied became permanently 55 cm. long, thus taking out any small bends which lay in this part of the wire before the stretching. Then we readjusted the wire on the rack in such a way as to bring opposite the 25 cm. mark of the meter-rod the same point of the wire which had previously been there and to bring opposite the 80 cm. mark of the rod the same point of the wire which had previously been opposite the 75 cm. mark. Then we made a test as before, touching the ice first at the 25 cm. point, then at the 26.1 cm. point, then at the 27.2 cm. point, and so on, by stages of 1.1 cm., to the 80 cm. point, thus trying to get at the same points in the wire which had been used before the stretching. It is to be noted, however, that a wire stretched through the whole of

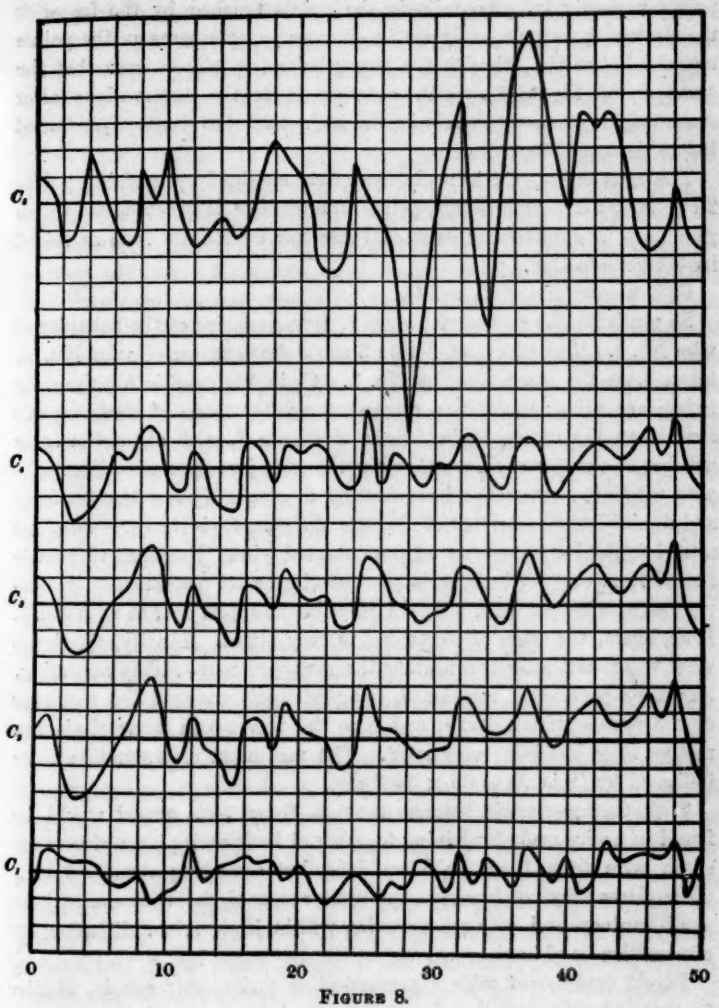

FIGURE 8.

its length at once is not necessarily stretched equally at all parts; for example, the point which had been the 50 cm. point before the stretching might not lie, and in our observations usually did not lie, just half-way between the points which had been the 25 cm. and the 75 cm.

points respectively. Accordingly the points touched by the ice after the stretching were probably not in all cases just the same as the points touched before the stretching. Nevertheless, it will be seen that the curve C_4 of Figure 7, which corresponds to the observations after stretching, agrees very closely in the main with the curve C_3 obtained before the stretching.

The next curve, C_5, is made from data obtained by touching points 25.5, 26.6, 27.7, etc.; that is, points intermediate between those which gave C_4. The differences between these two curves are such as might have been expected.

C_6 is a composite of C_4 and C_5.

So much for the curves of Figure 7, representative of the behavior of wire No. 1. The curves of Figure 8 show the behavior of wire No. 2, taken from the same piece as No. 1. C_1 in Figure 8 is for the state before annealing; it shows a somewhat smaller range of electromotive force than the corresponding curve of Figure 7, with about the same number of changes of sign. C_2 is for the state just after annealing. As with wire No. 1, annealing has increased the range of electromotive force and diminished the number of changes of sign. C_3 is the curve obtained after brightening the surface of the annealed wire. It differs very little indeed from C_2. C_4 is from the data obtained after permanently stretching the wire 10 per cent, a 50 cm. piece becoming 55 cm., as with No. 1. Here, again, the effect of stretching is very slight. Finally, C_5 shows what was found after reannealing the stretched wire. This annealing, like those previously mentioned, has profoundly changed the character of the representative curve; and here the increase in range of electromotive force has been very great. The maximum electromotive force indicated by C_5 is about 65×10^{-6} volt.

Such thermo-electric heterogeneity as these tests reveal would be found in a wire made by joining together at their ends pieces of german-silver wire from 1 cm. to 6 cm. long, but averaging about 2.5 cm., these pieces varying through some little range of chemical composition or of hardness and each piece having within itself minor differences of composition or of hardness.

Direct experiment with a german-silver and copper couple, similar to those already described in diameter and condition of wire, showed that, when one junction of such a couple is touched with a sharp edge of ice, the temperature of the room being near 18° C., the thermo-electromotive force developed is about 284×10^{-6} volt, about 450 times the maximum indicated by the curve C_5 in Figure 8. As the room temperature

when the data for this curve were taken may have been as high as 20°, we will take 500 as the ratio of the electromotive force of a (copper)-(german-silver) couple to that of the most effective (german-silver)-(german-silver) couple which could be made from contiguous parts of the wire which gave the curve C_g, the temperatures to be the same in both couples.

When one junction of this (copper)-(german-silver) couple was in contact with an ice surface about 1 cm. wide, so that contact between metal and ice extended about 0.5 cm. in each direction from the junction, the electromotive force developed was about 3 per cent greater than when a sharp edge only of ice was used, which may be taken as indicating that the sharp edge cools the junction to the neighborhood of 0°.5.

When the german-silver wire was touched by a sharp edge of ice at a distance of 1 cm. from a junction, the electromotive force was such as to indicate that the junction itself was thereby cooled about 3 degrees. Of course the junction, having the highly conducting copper on one side, was cooled somewhat less in this case than a similarly placed point in a continuous german-silver wire would have been. When the copper wire was touched by the edge of ice at a point distant 1 cm. from the junction, the junction was apparently cooled about 12 degrees.

It appears, then, that in our experiments along a straight piece of german-silver wire, exposed to the air of a room at 18° C., the point in contact with the sharp edge of ice was near the temperature 0°.5, while the points a centimeter distant from the point of contact were, perhaps, near the temperature 13°, the mean temperature gradient for the first centimeter in each direction from the point of contact being, therefore, let us say, 12°.

We may, for present purposes, safely regard the temperature change caused by the edge of ice as insensible at 2 cm. from the point of contact. The thermo-electromotive force caused by the inequality of temperature due to the ice is, therefore, dependent on the difference of thermo-electric quality of two pieces of wire, each 2 cm. long, which extend in opposite directions from the point of contact with the ice, and in each of which there is a temperature range of about 18°. Let us call these pieces section l and section r, respectively. The thermo-electromotive force under discussion is equal to the change of electromotive force which would result in one of our ordinary (copper)-(german-silver) couples, if we were to cut out a piece of german-silver having the quality of section l and substitute for it a piece having the quality of section r, the temperatures at the two points of cutting and joining being, approximately, 0° C. and 18° C., respectively.

When we are testing our couples with junction temperatures of, let us say, 140° and 180°, respectively, the german-silver wire between the vapor pots being freely exposed to the air or contained in glass tubes freely exposed to the air, we must have a very steep gradient of temperature in those parts of the wire which lie near the entrance to the pots. If near one pot there happens to be a section of german-silver wire 3 or 4 centimeters long having within itself a range of, let us say, 80°, and if the thermo-electric quality of this section differs from the mean thermo-electric quality of the wire one half as much as certain contiguous sections differ in the wire which gave the data for Figure 8, the electromotive force of the circuit as a whole, when the difference of temperature between the (copper)-(german-silver) junctions is 40°, will be about $\frac{1}{8}$ per cent greater or less than it would be if the given section were of average quality. If this differential effect assists the current when the neighboring (copper)-(german-silver) junction is the hotter one, it will oppose the current when this junction is the cooler one, thus making the difference between the "parallel" arrangement current and the "crossed" arrangement current $\frac{2}{8}$ per cent. If there is, as there may happen to be, near the other pot an equally eccentric section of wire, its eccentricity being of the opposite sign, we may get a difference between "parallel" and "crossed" amounting to $\frac{4}{8}$ per cent.

This goes some distance toward accounting for such difference (P — C) as we have observed, but it goes hardly far enough. The mean of the arithmetical values of (P — C) with the temperature interval 140° to 180° is about 1.3 per cent for the couples A_2, B_2, C_2, D_2, and, if we confine ourselves to observations thus far mentioned, about 3 per cent for the couples A_3, B_3, C_3, D_3. With couple C_3 on September 26 (P — C) was more than 5 per cent of the mean effect. It seems doubtful whether so great a discrepancy can reasonably be accounted for by such heterogeneity as exists in a freshly annealed wire; but the results of certain later calibration tests, now to be described, tend strongly to confirm the opinion that the (P — C) value is due in some way to the condition of the german-silver wire between the pots.

Further Calibration Tests of Couples A_3, B_3, C_3, and D_3.

We made on October 28 another calibration test with couples A_3, B_3, C_3, and D_3, in which we tried to keep the upper parts of the glass tubes containing the german-silver wires in a state of temperature intermediate between the temperatures of the two pots, about 100° and 218°, respectively. With this purpose we closed in the air space about

these tubes with shields of asbestos and cotton, thus leaving it to be heated from the tops of the pots. The temperature attained in the middle of this air space was perhaps 100°, not so high as we wished it to be, and we were far from getting a uniform temperature gradient in the wires leading from one pot to the other. At any rate, the performance of the couples in this trial was very little if any more harmonious than it had been on September 29, when no care had been taken to keep the parts in question warm. On the other hand, the mean electromotive force found on October 28 was about $\frac{3}{4}$ per cent less than it had usually been with the same interval of terminal temperatures.

Having now come to the conclusion that the arched [3] glass tubes, containing the german-silver wires between the pots, were an obstacle to the attainment of the temperature condition desired in this part of the apparatus, we now cut out these connecting parts of the glass tubes, thereby returning to an arrangement very like that shown in Figure 1. Placing the pots as near together as they could well be, we surrounded their tops with an elliptical wall of asbestos board, within which we placed loose asbestos fibre. Within this bed of asbestos ran the german-silver wires from pot to pot, each wire being covered to a depth of some centimeters. As the space from pot to pot was shorter for couples B_3 and C_3 than for A_3 and D_3, the junctions of B_3 and C_3 were let down into the pots two or three centimeters farther than those of the other couples.

With this arrangement, calibration tests were made on December 16 and 20 with a new interval, 180° to 218°, approximately. The high mean temperature of the junctions and the comparatively small interval of temperature would naturally have given still larger values of (P — C) than we had commonly found, even with the 140° to 180° interval, if we had not taken care to shield and warm the middle parts of the german-silver wires. More care in this regard was taken on December 20 than on December 16. The term (P — C) is not strictly applicable to the tests of these two days; for, both pots containing naphthalin, the reversal of conditions was effected not by changing from "parallel" to "crossed" or *vice versa*, but by making first the north pot and then the south pot the hotter, or *vice versa*. We shall therefore use the term (N — S) instead of (P — C). The summaries of galvanometer deflections for the two days are as follows:

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[3] We should probably have done well to retain these connecting parts of the tubes, reducing the arch as much as possible so as to bring the wires down near the tops of the pots.

	A_3 (N − S)	B_3 (N − S)	C_3 (N − S)	D_3 (N − S)
Dec. 16	$21.20_{(0.24)}^{+}$	$21.03_{(0.45)}^{+}$	$20.89_{(0.29)}^{+}$	$20.97_{(0.16)}^{-}$
" 20	$22.10_{(0.05)}^{+}$	$21.93_{(0.20)}^{+}$	$21.75_{(0.26)}^{+}$	$21.83_{(0.15)}^{-}$

The mean of the numerical values of (N − S) is 0.29, about 1.4 per cent of the deflection, for December 16, and 0.17, about 0.8 per cent of the deflection, for December 20.

On December 22 and 23 calibration tests were made with the temperature interval 100° to 140°, approximately. Both of the pots used on these days contained water, and the reversal of temperature conditions was effected, as on December 16 and 20, by having first one and then the other of the pots the hotter. The usual summary is as follows:

	A_3 (N − S)	B_3 (N − S)	C_3 (N − S)	D_3 (N − S)
Dec. 22	$19.76_{(0.00)}$	$19.58_{(0.16)}^{-}$	$19.36_{(0.11)}^{-}$	$19.44_{(0.16)}^{-}$
" 23	$19.78_{(0.07)}^{-}$	$19.60_{(0.20)}^{-}$	$19.39_{(0.19)}^{-}$	$19.50_{(0.21)}^{-}$

The mean of the numerical values of (N − S) is 0.105, about 0.5 per cent of the deflection, for December 22; and 0.17, about 0.9 per cent of the deflection, for December 23. Nearly all the (N − S) values of these two days have the minus sign, whereas on December 16 and 20 the plus sign prevailed. But the fact is that on the two earlier days the "crossed" arrangement existed, whereas on the two later days the "parallel" arrangement was used.

Finally, on December 28, a test was made with the interval 140° to 180°, appproximately, one pot now containing water and the other naphthalin, as in the early experiments. The result was:

A_3 (P − C)	B_3 (P − C)	C_3 (P − C)	D_3 (P − C)
$20.30_{(0.06)}^{+}$	$20.19_{(0.14)}^{+}$	$19.96_{(0.22)}^{+}$	$20.01_{(0.01)}^{-}$

The mean of the numerical values of (P − C) is here 0.11, about 0.5 per cent of the deflection.

The differential percentages, (N − S) or (P − C), found on these last five days of the calibration tests of couples A_3, B_3, C_3, and D_3, have a mean of 0.8 per cent. The temperature interval on each of these days was not far from 40°. The corresponding mean for previous tests of the same couples made with a like interval of temperature is 3 per cent. It is plain, then, that the policy of keeping the middle parts of the

german-silver wires warm is fully justified. It is doubtful whether on any day these parts were kept warmer than the top of the cooler of the two pots. It is reasonable to believe that, if an approximately uniform gradient of temperature had been maintained in these parts from one pot to the other, the differential percentage would have been reduced still further.

The Absolute Values of the Electromotive Force of the Couples.

In the following table, (2) indicates that the observations were made on couples A_2, B_2, etc.; (3) indicates that they were made with A_3, B_3, etc. The column Max. ÷ Min. gives the ratio of the highest mean electromotive force shown by any couple to the lowest mean electromotive force shown by any couple on the day considered. Results obtained before July 21 are omitted from this table because of some uncertainty as to the reduction factor of the galvanometer previous to this date. Results obtained after September are separated from those obtained earlier, because in the experiments made after September the policy of keeping the middle parts of the german-silver wires warm was followed, whereas in earlier experiments practically the opposite policy was maintained.

Date.	Set of Couples.	Temp. Interval.	Max. / Min.		Mean e. m. f. (volt) per Degree.	
July 21, 1905	(2)	140°.10 to 180°.36	A ÷ C = 1.004	1.004	2382 × 10^{-8}	2386
" 22 "	"	140°.14 " 180°.35	" = 1.003		2386 "	
" 24 "	"	140°.10 " 180°.50	D ÷ C = 1.004		2389 "	
Sept. 26 "	(3)	140°.20 " 180°.30	A ÷ C = 1.014	1.014	2375 "	2385
" 28 "	(3)	140°.10 " 180°.20	" = 1.013		2394 "	
		140°.13 " 180°.34			2385 "	
Sept. 22, 1905	(3)	140°.10 to 217°.80	A ÷ C = 1.010		2484 × 10^{-8}	
" 23 "	"	140°.10 " 217°.90	" = 1.014		2475 "	
" 25 "	"	140°.00 " 217°.90	" = 1.011		2472 "	
		140°.07 " 217°.87	1.012		2477 "	
July 25, 1905	(2)	99°.90 to 217°.90	D ÷ C = 1.004	1.004	2379 × 10^{-8}	
" 26 "	"	100°.00 " 218°.00	" = 1.004		2380 "	
" 29 "	(3)	100°.00 " 218°.00	A ÷ C = 1.005	1.007	2389 "	
Aug. 3 "	"	100°.00 " 218°.10	" = 1.005		2385 "	
Sept. 29 "	"	100°.10 " 218°.20	" = 1.010		2389 "	
		100°.00 " 218°.04			2385 "	

From this table we get, by reductions which need not be detailed:

Temp. Interval.	Total e. m. f.	Mean e. m. f. per Degree.
140° to 180°	9536×10^{-7}	2384×10^{-8}
140° " 218°	19320 "	2477 "
100° " 218°	28140 "	2385 "

From these reduced values we get:

α = total e. m. f. from 100° to 140° = 8820×10^{-7}
β = " " " 140° " 180° = 9536 "
γ = " " " 180° " 218° = 9784 "
Hence $\alpha + \beta + \gamma = 28140$ "

Taking now the results obtained after September, except those of December 2, which are rejected because of strong evidence that uniform temperature conditions were not maintained, we have

Date.	Set of Couples.	Temp. Interval.	Max. / Min.	Mean e. m. f. (volt) per Degree.
Oct. 28, 1905	(3)	100°.30 to 218°.60	$A \div C = 1.011$	2375×10^{-8}
Dec. 16	"	" 180°.35 " 218°.53	" $= 1.015$	2543 "
" 20	"	" 179°.77 " 218°.63	" $= 1.016$	2545 "
" 22	"	" 99°.93 " 140°.07	" $= 1.021$	2176 "
" 23	"	" 99°.75 " 140°.02	" $= 1.020$	2178 "
" 28	"	" 140°.25 " 180°.13	" $= 1.017$	2362 "

From these values we get:

Dec. 22 and 23 α = total e. m. f. from 100° to 140° = 8708×10^{-7}
" 28 β = " " " 140° " 180° = 9444 "
" 16 and 20 γ = " " " 180° " 218° = 9660 "
Hence $\alpha + \beta + \gamma = 27812$ "

Oct. 28 $\alpha + \beta + \gamma$ = total e.m.f. from 100° to 218° = 28000

Giving to the value of $\alpha + \beta + \gamma$ found on October 28 one half as much weight as to the value found by combining the December results, and revising the December values of α, β, and γ accordingly, we get:

		Mean e. m. f. per Degree.
α (before Oct. 1) = 8820×10^{-7} " (after " ") = 8728 "	8774×10^{-7}	2194×10^{-8}
β (before " ") = 9536 " " (after " ") = 9466 "	9500 "	2375 "
γ (before " ") = 9784 " " (after " ") = 9683 "	9734 "	2562 "

The values obtained before the policy of heating the middle of german-silver wires was adopted are at every stage somewhat greater, and on the average about 1 per cent greater, than those given by the later experiments. The reason for this is not apparent. It seems best to take the mean value for each stage. The numbers thus obtained indicate a nearly uniform increase of "thermo-electric height," electromotive force for 1° difference of temperature of the junctions, for the interval from 100° to 218°. Perfectly uniform increase would require the values found for the 140° to 180° region to be raised about 1 in 400.

If we take 2194×10^{-8} as the thermo-electric height for 120°, the middle of the α interval, and 2562×10^{-8} as the thermo-electric height for 199°, the middle of the γ region, we get 4.7×10^{-8} as the mean increase per degree from 120° to 199°. This rate of change applied downward from 120° would give 2100×10^{-8} as the thermo-electric height for 100°.

At the end of the paper[4] referred to at the beginning of this article a summary is given of the results of calibration experiments on sets of thermo-electric couples other than those here studied but made from the same materials in the same way. From this summary we get

$$\text{thermo-electric height at } 89°.4 = 2063 \times 10^{-8}$$
$$\text{" " " " } 17°.4 = 1713 \text{ "}$$

From these values we get 4.9×10^{-8} as the rate of increase per degree from 17°.4 to 89°.4. This rate continued gives 2115×10^{-8} as the thermo-electric height at 100°. This differs about 0.7 per cent from the value found above. The value for 199° calculated from the data obtained in the region below 100° would be 2600×10^{-8}, only 1.5 per cent greater than the value found in this paper.

Taking 2100×10^{-8} as the thermo-electric height at 100° and taking the rate of increase per degree rise of temperature as 4.8×10^{-8}, we should get values which would not at any point between 0° and 218° differ as much as 1 per cent from the most probable value which we have for that point.

It has been stated earlier in this paper that in the (2) set of couples the maximum difference of mean electromotive force among the various couples was about 0.3 per cent of the mean electromotive force. The corresponding difference was greater in the (3) set of couples, being, on

[4] These Proceedings, May, 1905.

the average, perhaps as much as 1.5 per cent of the mean electromotive force, and amounting in some cases to 2 per cent. This difference seemed to grow greater in set (3) as time passed, for at the start, in July, it was only about 0.5 per cent. This change may have been due to changes in the method of experimenting or to some more or less damaging experiences which the couples had suffered in some months of existence and many days of use. It is difficult, especially when the german-silver wire is not protected along its middle by tubing, to prevent an occasional accidental pull which may stretch some part permanently a little and thus change its thermo-electric quality. We know that a couple made of hard-drawn german-silver with copper is 3 or 4 per cent more powerful than a couple made of the annealed german-silver wire with copper.

On this point certain experiments made December 6 and 7, 1905, have a bearing. Four pieces of carefully annealed german-silver wire were each stretched to a permanent extension of 10 per cent in one part, and then the stretched part of each was used with the unstretched part of the same wire as a thermo-electric couple. The mean thermo-electric force of the four couples thus formed was found to be about 0.6 per cent of that of a couple made with copper and the annealed german-silver. The stretching, which hardened the wire somewhat, thus bringing it slightly toward the hard-drawn condition, changed its thermo-electric quality slightly toward that of hard-drawn wire. If slightly different annealing currents or slightly different periods of application of such currents can leave different pieces of wire as unlike as the stretched and the unstretched pieces here tested, the observed differences of sensitiveness of the couples A_3, B_3, C_3, and D_3 may be due, in considerable measure, to such inequalities.

If we were now making a new set of couples, we should take more care than we have usually taken heretofore to have all the pieces of german-silver wire heated by the same strength of current and for the same number of seconds. A current of 3 amperes applied for 5 seconds is suitable for german-silver wire such as we have used. This wire is about 0.02 cm. in diameter, being No. 32 of the Brown and Sharpe gauge.

Behavior of Manganin and of Constantin.

The thermo-electric heterogeneity shown in german-silver by some of the tests which have been described in the preceding pages induced us to make somewhat similar tests with manganin and with constantin.

A piece of annealed manganin wire 0.205 cm. in diameter was drawn

down without further annealing to a diameter of 0.051 cm. It was then tested, by touching with ice, as the german-silver wire had been tested, first in the hard-drawn condition, then in the annealed condition, then after rubbing bright, then after stretching. The results, in general character and in magnitude of the local electromotive forces developed, were similar to those found with german-silver, though no eccentricity so great as that indicated by certain parts of the curve C_3 in Figure 8 was developed. Annealing increased the local eccentricities. Stretching affected them but little. The maxima and minima appeared to be somewhat less numerous than in the german-silver wires. The curve obtained after brightening differed considerably from that found before brightening, but as six days intervened between the two tests which gave these curves, it is doubtful whether the change is to be attributed to the scouring alone.

A piece of constantin wire was drawn cold from a diameter of 0.051 cm. to a diameter of 0.036 cm., approximately. It was then tested, by touching with ice, in the hard-drawn condition, and later in the annealed condition, the annealing being done, as in the case of german-silver and of manganin, by heating to incandescence for a few seconds by means of an electric current. The local electromotive forces found were very small, perhaps one fifth as large as those in german-silver and in manganin, and indeed the difficulty of determining their size was so great that the wire was tested in two conditions only. The maxima and minima appeared to be about as frequent as in german-silver. Annealing changed the character of the representative curve, but did not increase its eccentricities.

It might be suspected that the constantin wire, being nearly twice as large in diameter as the german-silver wire, might not be so much affected locally in temperature by contact with the edge of the ice. Experiments made December 26 showed this idea to be without foundation. The edge of ice cooled a copper-constantin junction as effectually as it would cool the smaller (copper)-(german-silver) junction; when placed 1 cm. distant from the junction along the constantin it produced about one eighth part as great an effect as when applied at the junction; at 1.5 cm. from the junction along the constantin the effect was about 3 per cent of that at the junction. On the other hand, when the edge of ice was applied at a distance of 25 cm. from the junction along the copper wire, 0.036 cm. in diameter, its effect was still perceptible, being apparently more than 1 per cent as great as the effect produced by applying the

ice directly to the junction. In these tests the wire between the ice and the junction was in free air at the temperature of the room, about 16°C.

Experiment showed that a couple made of copper and unannealed constantin had an electromotive force about 1.5 per cent greater than that of a couple made of copper and annealed constantin, from the same original piece as the unannealed.

The electromotive force of a copper-constantin couple for a given interval of temperature near the temperature of the room is two or three times as great as that of a (copper)-(german-silver) couple under like conditions.

So far, then, as our tests go, it appears that in every particular constantin is a better metal than german-silver to use thermo-electrically with copper, but we have tested only one specimen of constantin.

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